Geo-Note 2004-04

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Comparison of Field-Portable X-Ray Fluorescence Analyzer and Conventional Geochemical Analysis

Alberta Energy and Utilities Board
Alberta Geological Survey

106-00116/

Comparison of Field-Portable X-Ray Fluorescence Analyzer and Conventional Geochemical Analysis

D. Roy Eccles[1] and Ed Murphy[2]

[1]Alberta Geological Survey
[2]Elemental Controls Ltd.

March 2005

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ISBN 0-7785-3836-2

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Eccles, D.R. and Murphy, E. (2005): Comparison of field-portable x-ray fluorescence analyzer and conventional geochemical analysis; Alberta Energy and Utilities Board, EUB/AGS Geo-Note 2004-04.

Author Address:
Ed Murphy
Elemental Controls Ltd.
3230 Wharton Way
Mississauga, ON L4X 2C1
(905) 282-9974
E-mail: emurphy@elementalcontrols.com

Published March 2005 by:
Alberta Energy and Utilities Board
Alberta Geological Survey
4th Floor, Twin Atria Building
4999 – 98th Avenue
Edmonton, Alberta
T6B 2X3

Tel: (780) 422-3767 (Information Sales)
Fax: (780) 422-1918

Website: www.ags.gov.ab.ca

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Acknowledgments

This study was completed as part of a Geological Survey of Canada Targeted Geoscience Initiative to investigate the potential for carbonate-hosted lead-zinc (Pb-Zn) deposits in northern Alberta and southern Northwest Territories. As such, the portable XRF analyzer test was developed in consultation with the Geological Survey of Canada and C.S. Lord Northern Geoscience Centre in Yellowknife, Northwest Territories.

Several individuals provided sample material and essentially made this study possible. Special thanks to

- Suzanne Paradis and Keith Dewing of the Geological Survey of Canada, for samples from the Robb Lake Deposit, BC, and Pb-Zn occurrences from Ellesmere Island and Cornwallis Island, respectively;
- Allan Turner for pointing us to the location of samples from the Pine Point Deposit, NWT, and the University of Alberta for providing the necessary logistics to sample the Pine Point core; and
- Jennifer Adams (then of the Alberta Geological Survey) for a sample of Alberta dolomite.

We also thank Randy Rice and Dinu Pana of the Alberta Geological Survey (AGS); David Seneshen, formerly of AGS but is now in private industry; and Peter Hannigan and Keith Dewing, Geological Survey of Canada, for participating in the test. Reg Olson, AGS, and Eric Grunsky, formerly of AGS but now with the GSC in Ottawa, are thanked for editing the manuscript and providing valuable comments.

The portable XRF analysis test was conducted at the Alberta Energy and Utilities Board Core Research Centre in Calgary, Alberta, and we thank Laurie Wilcox for her always-gracious help and advice.

Abstract

A total of 39 rock (hand-sized grab and core) samples were analyzed as part of a geochemical test to compare the quantitative measurements between the field-portable x-ray fluorescence (XRF) analyzer versus conventional geochemical analysis. Samples with variable amounts of sulphides, ranging from massive sulphide to partially mineralized and three certified reference sample standards (MP-1A ore) prepared by CANMET, were used. The study, which was conducted as part of a carbonate-hosted Mississippi Valley-type lead-zinc deposit project, used selected samples from deposits and occurrences of lead and zinc only. Thus, the results of the study focus primarily on these base metals, plus iron, rather than on a more extensive suite of base and precious metal elements.

A portable Niton XL-502S XRF analyzer was compared with conventional geochemical methods, which included total digestion Induction Coupled Plasma – Atomic Emission Spectrometer (ICP-ES) and x-ray fluorescence.

The portable XRF analyzer exhibited high analytical precision for the elements lead, zinc and iron. When compared with ICP-ES analysis, a linear correlation coefficient (r^2) of between 95% and 100% was determined for powdered XRF analysis, and an r^2 of between 79% and 89% for spot XRF analysis (i.e., random 'spot' analyses directly on the rock and core specimens). Thus, it is concluded that the Niton XRF analyzer produces quick and efficient screening assays and analytical results of greater precision by powdering approximately 10 g of the sample.

Finally, as the portable XRF analyzer technique evolves and a larger suite of elements with lower limits of detection become available, the tool will become more useful in reconnaissance-type fieldwork. It will also have significant benefit in core libraries, especially if real-time core logging coupled with immediate semi-quantitative results is sought.

1 Introduction

Like conventional laboratory geochemical techniques, the field-portable x-ray fluorescence (XRF) may be used for measuring metal concentrations in a variety of sample media, including soil, sediment, rock and drillcore. However, the versatility of the portable XRF, coupled with time efficient sample preparation and analysis to obtain semi-quantitative results, may provide a suitable technique for the quick evaluation of samples in the field and/or at core libraries.

The Alberta Geological Survey (AGS), in conjunction with Elemental Controls Ltd., conducted a test using various cores and hand-sized rock samples to evaluate the quantitative measuring comparability of the field-portable x-ray fluorescence versus conventional geochemical analysis.

As part of a project to evaluate the potential for carbonate-hosted Mississippi Valley-type lead-zinc (Pb-Zn) deposits in northern Alberta and south-central Northwest Territories, a sample suite from various Pb-Zn deposits and occurrences was selected for testing.

If the results of the test show that the XRF analyzer data are comparable to data from standard geochemical analysis, the portable XRF unit will be of benefit to industry and government in both the field and office environments. In addition, the portable analyzer may be particularly useful at core facilities, given the high volume of core typically stored in core warehouses. Also, because little or no sample material is required for the XRF analyzer, the core can be preserved for future use.

2 Methodology

2.1 Sample Selection and Preparation

A total of 39 rock (hand-sized grab and core) samples were analyzed by the portable XRF and by conventional geochemical analysis. A description of each sample and a ranking on the homogeneity of each sample is provided in Table 1.

Because the study was conducted as part of the carbonate-hosted Mississippi Valley-type Pb-Zn deposit study, selected samples are from deposits and occurrences of lead and zinc only. Thus, the results of the study focus on these base metals, and iron, rather than on a more extensive suite of base and precious metal elements.

To test a wide spectrum of Pb-Zn content, we included samples with variable amounts of sulphides, ranging from Pb-Zn deposits with massive sulphide (>80% galena and sphalerite), to trace sulphide (<5%) samples adjacent to Pb-Zn deposits, and selected oil or gas wellcore that has reportedly high Pb or Zn contents relative to known average concentrations in Paleozoic sedimentary rocks of northern Alberta. A breakdown of the sample sources include

- four samples from northeast Ellesmere Island, NWT;
- one sample from Victor Creek, Cornwallis Island, NWT;
- nine samples from the Pine Point deposits, NWT;
- ten samples from the Robb Lake deposits, BC;
- one sample from the Cambrian strata of western Alberta; and
- six samples from wellcore in northern Alberta that was reported by Turner and McPhee (1994) to contain high concentrations of Pb-Zn (up to 37 633 ppm Zn and 1064 ppm Pb).

Table 1. General description and homogeneity rank of samples selected for the XRF analyzer test.

AGS_ID	Deposit/site	General lithology	Mineralization	Homogeneity (1-homo to 3-poly)
RE01-MVT-XRF-001	NE Ellesmere Island	Medium grey, medium-grained, crystalline, vuggy dolomite/carbonate/calcite?	Trace (2 to 5%) malachite	2 - mottled dolomite+calcite
RE01-MVT-XRF-002	NE Ellesmere Island	Medium Grey, fine-grained, sub-crystalline dolomite with 10% black styolites	3% medium-grained chalcopyrite+calcite+sphalerite	3 - mottled with calcite veinlets
RE01-MVT-XRF-003	NE Ellesmere Island	White and brown speckled, coarse-grained, crystalline quartz (60%) and dark brown siderite (40%)	No sulphides	3
RE01-MVT-XRF-004	NE Ellesmere Island	Black, fine-grained, fissile, slaty shale	Fine-grained pyrite (5%)	1
RE01-MVT-XRF-005	Victor Creek, Cornwallis Island	Medium Brown, fine-grained, massive dolostone with minor calcite veinlets	None	1
RE01-MVT-XRF-006	Pine Point	Massive to semi-massive galena+sphalerite+carbonate	40% sphalerite, 30% galena and 30% carbonate fossils	3
RE01-MVT-XRF-007	Pine Point	Buff-coloured, fine-grained dolostone with 5% white calcite veinlets	No sulphides	1
RE01-MVT-XRF-008	Pine Point	medium Grey, fine-grained dolostone	No sulphides	1
RE01-MVT-XRF-009	Pine Point	Massive, fine-grained mudstone	No sulphides	1
RE01-MVT-XRF-010	Pine Point	medium Brown, fine-grained dolostone	10% sphalerite+galena	2
RE01-MVT-XRF-011	Pine Point	Semi-massive, medium-grained sulphide with calcite/dolomite groundmass	40% sulphide (galena>sphalerite)	2
RE01-MVT-XRF-012	Pine Point	Dark grey, massive sulphide	50% galena, 40% sphalerite and 10% dolomite	2
RE01-MVT-XRF-013	Pine Point	Grey and white, mottled, fine grained, grey dolomite and medium-grained crystalline calcite	No sulphides	3
RE01-MVT-XRF-014	Pine Point	Grey, fine-grained, sugary textured crystalline dolostone	5% medium-grained honey-coloured sphalerite	2
RE01-MVT-XRF-015	Rob Lake	Brown and grey mottled massive sulphide	80% sphalerite, 5% galena and 15% carbonate matrix	3
RE01-MVT-XRF-016	Rob Lake	Late stage white calcite with grey dolomite	Abundant (20%) sphalerite, minor galena	3
RE01-MVT-XRF-017	Rob Lake	Late stage white calcite with grey dolomite fragments	Minor (<5%) visible galena	3
RE01-MVT-XRF-018	Rob Lake	Late stage white calcite and grey dolomite fragments	Trace (2%) sphalerite and galena	3
RE01-MVT-XRF-019	Rob Lake	Late stage white calcite and grey dolomite fragments	Galena and red (garnet?) in late calcite dolomite	3
RE01-MVT-XRF-020	Rob Lake	Late stage white calcite with angular grey dolomite fragments	Sphalerite?, red-carbonate?, MgCO3?	3
RE01-MVT-XRF-021	Rnb Lake	Dolostone and veins/blebs of secondary calcite	2-3% sphalerite	2 - patchy sulphides
RE01-MVT-XRF-022	Rob Lake	Late calcite, maybe minor dolomite	Trace (2%) sphalerite and galena	3
RE01-MVT-XRF-023	Rob Lake	Fragmented light-grey and dark-grey dolomite with lesser late stage calcite	Trace (2%) sphalerite and galena	2 - breccia or collapse
RE01-MVT-XRF-024	Rob Lake	Grey-dolomite with late-stage calcite	No sulphides	3
RE01-MVT-XRF-025	Alberta	Zebra dolomite	No sulphides	3
RE01-MVT-XRF-026	Alberta	Dark-grey sheared dolomite	Abundant (20%) sphalerite	3
RE01-MVT-XRF-027	Alberta	Medium Grey and dark grey dolomite	Minor (<5%) sphalerite	2
RE01-MVT-XRF-028	Alberta	Fragmented grey-white calcite, possibly grey dolomite	No sulphides	3
RE01-MVT-XRF-029	Alberta	Buff-coloured dolomite, possible bioturbation	No sulphides	1
RE01-MVT-XRF-030	Alberta	Light brown dolomite with grey sub-rounded dolomite?	No sulphides	2
RE01-MVT-XRF-031	Alberta	Light grey and light brown dolomite with diagenetic textures	Minor (<5%) replacement sulphide blebs	2
RE01-MVT-XRF-032	MP-1A Certified Reference Ore			
RE01-MVT-XRF-033	Duplicate of -001			
RE01-MVT-XRF-034	Duplicate of -016			
RE01-MVT-XRF-035	Duplicate of -020			
RE01-MVT-XRF-036	MP-1A Certified Reference Ore			
RE01-MVT-XRF-037	Duplicate of -024			
RE01-MVT-XRF-038	Duplicate of -025			
RE01-MVT-XRF-039	MP-1A Certified Reference Ore			

In addition to the 31 samples listed above, we analyzed five randomly selected duplicate samples and three certified reference samples (MP-1A ore), which were prepared by CANMET, for a total of 39 samples. The samples, which generally weighed between 100 and 900 g, were split in half by placing the sample in a plastic bag and hammering the sample. One half (generally the largest piece) of the sample was retained for 'spot analysis' by directly placing the portable XRF analyzer on the rock. The other half of the sample was crushed to –150 mesh using a ceramic mortar and pestle. The five duplicates were taken from the pulverized material. The certified reference sample (MP-1A ore) was already provided in a pulverized form by CANMET.

In preparation for the test, we laid out a station for each sample with the original (non-pulverized) rock sample for spot analysis and a 10-g 'sample cup' of the pulverized material for powder analysis. The sample cups were prepared by

1. placing Mylar X-Ray Film over one end of a Chemplex XRF sample cup;
2. adding approximately 10 g of sample material;
3. adding enough synthetic fibre batting to the open end of the plastic cylinder to compress the sample material against the Mylar 'window'; and
4. snapping a plastic cap to the batting end of the sample cup to secure the contents.

2.2 Analytical Techniques

To compare a portable XRF analyzer with conventional geochemical analysis, we selected the Niton XL-502 S unit for the portable XRF analyzer, and total digestion Induction Coupled Plasma – Atomic Emission Spectrometer (ICP-ES) and X-Ray Fluorescence (XRF) for the conventional geochemical methods.

2.2.1 Field-Portable X-ray Fluorescence Analyzer

The Niton XL-500 Series portable XRF units are single-piece handheld analyzers that use x-ray fluorescence to analyze for a suite of standard elements. Depending on the isotope source (^{109}Cd, ^{55}Fe or ^{241}Am), mode of operation and unit software, the portable XRF unit can analyze for Mo, Nb, Zr, Bi, W, Pb, Zn, Cu, Ni, Co, Fe, Mn, Cr, Ti, V, U, Sn, Au, Ag, Pt, Rh, Ir and Pd. These analyzers are equipped with a high-resolution silicon PIN diode detector, which are thermoelectrically cooled, negating the need for cryogenic cooling, and operate at a resolution of approximately 230 electron volts. The portable analyzer displays a primary screen of elements that are within the 95% confidence band. The instrument is capable of storing and downloading up to 1000 assays with full spectral data.

The Niton XL 502S analyzer that was used in this test is equipped with a ^{109}Cd isotope source and uses NpL-shell emissions and the 23.0 gamma-ray emission to produce x-rays. This unit features essentially two modes of operation, both of which are consistent with the software utilized for internal calibration. These provide the capability for 'high range' Fundamental Parameters (FP) and 'low range' Compton Normalization (CN) element concentration assays. The CN mode quantifies elements in the concentration range 10 ppm to 20 000 ppm depending on the element. The FP mode, separately, quantifies elements in the range 0.1 wt % to 100 wt %.

For this geochemical test, the Niton XL 502 S was operated in FP mode to provide rapid-screening capability for economic minerals.

Both the rock and powdered samples are from the same specimen. The rock sample was analyzed by placing the exposure window of the portable analyzer, which measures 1.0 by 2.0 cm, directly onto

randomly selected areas of the rock. The analyzer was unable to analyze some of the rougher rock surfaces. This was not a major problem during our testing, although we recommend that, where possible, flat rock surfaces be selected for analysis. Up to four spot analyses (depending on the availability of rock surface area) were conducted on each rock sample. The powdered samples were analyzed by placing the exposure window of the portable analyzer directly onto the Mylar 'window' of the mineral-containing sample cup, which was held in a sample platform. The *in situ* (i.e., on the rock and core specimens) measurement times used during this study ranged from between 30 to 60 seconds.

2.2.2 Conventional Geochemical Analysis

For the FP mode used, the Niton portable XRF analyzer reported only the elements Pb, Zn and Fe within the 95% confidence level for concentrations >0.1 wt %. Hence, we only analyzed for Pb, Zn and Fe using ICP-ES and XRF laboratory geochemistry. Activation Laboratories Ltd. (ActLabs) of Ancaster, Ontario, completed the laboratory analysis.

The ICP-ES method is capable of determining the concentrations of 40 to 70 elements simultaneously by measuring the intensity of light given off by samples aspirated into an argon plasma heated to >10 000°K. The technique is capable of ultra-low detection limits (ppb to ppt) with very wide linear ranges (five orders of magnitude). The samples were subject to aqua regia digestion, and the ICP-ES analysis was performed on a Thermo Jarrell Ash Enviro II. The samples were analyzed over a four-day period. Calibration verification standard samples were run after each batch of 10 samples was analyzed. The analytical precision quoted by ActLabs is 3% for these analyses at 100 times the detection limit.

The XRF method determines major and trace elements by measuring secondary x-ray emission after a solid sample is bombarded with a primary x-ray beam. Elements have characteristic energy levels for secondary x-ray emission with the intensity of the emission characteristic of the concentration. X-ray fluorescence analysis was performed on a Philips PW 1400 XRF unit. Calibration verification standard samples were run after each batch of 20 samples was analyzed. The analytical precision quoted by ActLabs is 3% for these analyses at 100 times the detection limits.

3 Results

3.1 Analytical Precision

Lack of samples did not permit a rigorous statistical analysis and it is important to note, therefore, that a determination as to the analytical precision of the XRF analyzer inferred herein is based on a limited number of samples. For example, we are unable to characterize the normality of the distribution since only three certified reference samples from CANMET were used.

Nevertheless, we used the relative standard deviation (RSD) statistical method to evaluate the results for precision. The RSD is a measure of the relative dispersion of the values in a dataset and is calculated by dividing the standard deviation by the mean from a dataset (Le Maitre, 1982); the dividend is then multiplied by 100. Subsequently, the lower the RSD value, the higher the level of precision.

The RSD percentage for the duplicate analysis of five randomly selected separates and three certified reference samples from CANMET is presented in Table 2. Zinc and iron analysis by ICP-ES and portable XRF analyzer have relative errors up to <5.5% for Fe in sample duplicates by portable XRF analyzer, but with the other RDS percentages for Fe and Zn all being <2.3%. This suggests there is good analytical reproducibility between Lab ICP-ES and Portable XRF results for these two elements. In contrast, the

Table 2. Relative error of sample duplicates and the certified sample standards.

Sample No.	Certified sample ID or duplicate sample no.	Laboratory ICP-ES Pb (%)	Laboratory XRF Pb (%)	Portable XRF Pb (%)	CANMET by ICP Pb (%)	CANMET by XRF Pb (%)	Laboratory ICP-ES Zn (%)	Laboratory XRF Zn (%)	Portable XRF Zn (%)	CANMET by ICP Zn (%)	CANMET by XRF Zn (%)	Laboratory ICP-ES Fe (%)	Portable XRF Fe (%)	CANMET Fe (%)
Detection limit ---------->		0.00002	0.0005	0.1			0.00001	0.0005	0.1			0.000001	0.1	
RE01-MVT-XRF-032	MP-1a cert.[1]	3.859	>1.00	3.170	4.370	4.250	19.115	>1.00	18.060	18.560	18.600	5.610	5.580	6.200
RE01-MVT-XRF-033	Duplicate of -001	0.003	0.008	bild*			0.001	0.06	bild			0.095	bild	
RE01-MVT-XRF-001	Original -001	0.002	0.002	bild			bild	0.03	bild			0.092	bild	
RE01-MVT-XRF-034	Duplicate of -016	2.192	>1.00	bild			6.576	>1.00	5.560			0.560	0.570	
RE01-MVT-XRF-016	Original -016	2.230	>1.00	1.060			6.724	>1.00	5.680			0.580	0.520	
RE01-MVT-XRF-035	Duplicate-020	0.005	0.014	bild			5.445	>1.00	4.340			0.860	0.720	
RE01-MVT-XRF-020	Original -020	0.008	0.017	bild			5.651	>1.00	4.250			0.940	0.640	
RE01-MVT-XRF-036	MP-1a cert.	3.952	>1.00	2.750	4.370	4.250	19.120	>1.00	17.250	18.560	18.600	5.740	5.860	6.200
RE01-MVT-XRF-037	Duplicate of -024	0.107	0.096	bild			0.584	0.566	0.400			2.500	1.680	
RE01-MVT-XRF-024	Original -024	0.100	0.087	bild			0.519	0.481	0.420			2.495	1.780	
RE01-MVT-XRF-038	Duplicate of -025	0.002	0.004	bild			bild	0.02	bild			0.096	0.110	
RE01-MVT-XRF-025	Original -025	0.003	0.003	bild			0.017	0.008	bild			0.102	0.100	
RE01-MVT-XRF-039	MP-1a cert.	3.886	>1.00	3.160	4.370	4.250	18.785	>1.00	17.650	18.560	18.600	5.700	5.670	6.200
Certified standard	Standards - Mean	3.886	auld*	3.160			19.115	auld	17.650			5.700	5.670	
	Standards - Std. Dev.	0.048	auld	0.240			0.192	auld	0.405			0.067	0.143	
	RSD%[2]	1.231	auld	7.584			1.004	auld	2.295			1.188	2.521	
Sample duplicates	Duplicates - Mean	0.465	0.029	bild			2.550	0.194	2.065			0.832	0.612	
	Duplicates - Std. Dev.	0.007	0.003	bild			0.059	0.084	0.033			0.016	0.034	
	RSD%	1.474	11.632	bild			2.325	43.337	1.575			1.942	5.546	

[1] CANMET certified sample MP-1a

[2] Relative standard deviation (RSD%) = (Std. Dev./Mean)*100)

* bild = below the lower limit of detection

* auld = above the upper limit of detection

analytical reproducibility of the portable XRF analyzer for Pb was not as good; that is, all five duplicate samples contain Portable XRF Pb values below the lower limit of detection, and the certified sample standards have an RSD percentage of 7.6% for Pb.

The RSD for the laboratory XRF analysis was seemingly poor in comparison to the laboratory ICP and portable XRF analyses. That is, the laboratory XRF had an RSD percentage of between 12% and 43% for duplicate pairs. There are, or may be, several reasons for this, including

(a) the laboratory XRF method used did not provide analytical results above 1 wt. %, which thereby eliminated a comparison of laboratory XRF versus the certified standard results, and also several of the duplicate sample Pb and Zn results; and

(b) for many of the remaining sample duplicate Pb, and some of the sample duplicate Zn, analytical results were very low, equal or less than 0.01 wt. %.

Hence, even small differences (e.g., from 0.003 wt. % to 0.008 wt. % in RE01-MVT-XRF-033) between the methods caused large changes in any calculated RSD. In general, only one sample and its duplicate pair (i.e., RE01-MVT-XRF-024 and RE01-MVT-XRF-037, respectively) gave possibly meaningful comparisons for Pb and Zn. For example, (a) for Pb, the Lab ICP-ES results for these samples ranged from 0.100 wt. % to 0.107 wt. %, versus 0.087 to 0.096 wt. % from Lab XRF, and (b) for Zn, the Lab ICP-ES was 0.519 wt. % to 0.584 wt. %, the Lab XRF was 0.481 wt. % to 0.566 wt. %, and the Portable XRF results were 0.400 wt. % to 0.420 wt. %. In short, although the calculated RSD in Table 2 for Laboratory XRF results is high, they may in fact severely overstate the actual case. The geochemical data from duplicate and the certified reference samples are shown on the plot of values obtained by the ICP-ES method versus those obtained using the portable XRF analyzer (Figure 1). The geochemical data from the sample duplicates and certified reference standards for Zn (Figure 1B) and Fe (Figure 1C) show good correlation between sample pairs and a good overall positive linear trend, although in general, the Portable XRF results tend to be slightly lower than those reported by ICP-ES. It is hard to evaluate Pb (Figure 1A), since all sample duplicates are below the lower limit of detection of the XRF analyzer. Nonetheless, the Certified Standards do plot relatively close to the 1:1 correlation line, although again, the Portable XRF results are consistently lower than the ICP-ES PB results.

As a result of the above, and because the laboratory XRF method gave few reliably comparative results, we concluded this study should focus on a comparison between ICP-ES and the Niton portable XRF analyzer.

3.2 Geochemical Comparison between Laboratory ICP-ES and the Portable XRF Analyzer

The geochemical results of the survey are presented in Tables 3 and 4, and Figures 2 and 3. Table 3 and Figure 2 compare the results of the ICP-ES and XRF analyzer powder analysis. Table 4 and Figure 3 compare the results of the ICP-ES and XRF analyzer spot analysis.

At first glance, the most recognizable difference between the conventional ICP-ES analysis and the Niton portable XRF analyzer is the limit of detection capability of the portable XRF analyzer. The Niton portable XRF analyzer, in the FP mode, reported only the elements Pb, Zn and Fe within the 95% confidence level. That is, the portable XRF analyzer recorded no values for elements other than Pb, Zn and Fe, since these were all below the limits of detection for the FP high range concentration mode (i.e., <0.1%). It should be noted, however, that the Niton portable XRF analyzer has also the capability of determining a broad range of elements in the CN mode where the concentrations are below the detection limits of the FP Mode.

Figure 1. Portable XRF versus laboratory analysis for duplicates and certified standard samples

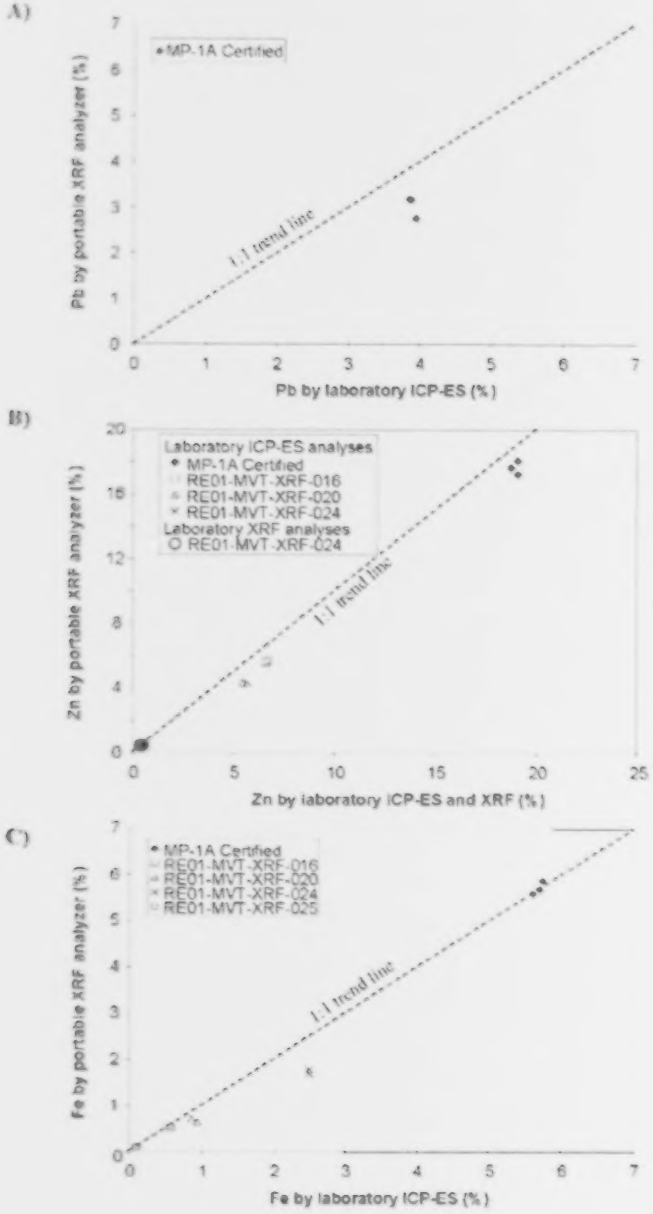


Table 3. Geochemical results from laboratory and portable XRF analyzer analyses using powdered samples.

Sample No.	Sample location	Laboratory ICP-ES Pb (%)	Laboratory XRF Pb (%)	Portable XRF Pb (%)	Laboratory ICP-ES Zn (%)	Laboratory XRF Zn (%)	Portable XRF Zn (%)	Laboratory ICP-ES Fe (%)	Portable XRF Fe (%)
Detection limit ---------->		**0.00002**	**0.0005**	**0.1**	**0.00001**	**0.0005**	**0.1**	**0.000001**	**0.1**
RE01-MVT-XRF-001	NE Ellesmere Island	0.002	0.002	blld*	blld	0.032	blld	0.092	blld
RE01-MVT-XRF-002	NE Ellesmere Island	0.014	0.009	blld	2.997	>1.0	2.250	2.750	1.690
RE01-MVT-XRF-003	NE Ellesmere Island	blld	0.001	blld	0.019	0.021	blld	5.704	5.020
RE01-MVT-XRF-004	NE Ellesmere Island	0.006	0.006	blld	0.007	0.011	blld	5.087	4.460
RE01-MVT-XRF-005	Victor Cr., Cornwallis Is.	0.003	0.001	blld	0.001	0.004	blld	0.027	blld
RE01-MVT-XRF-006	Pine Point	50.170	>1.0	28.110	25.130	>1.0	27.260	0.350	0.510
RE01-MVT-XRF-007	Pine Point	0.005	0.016	blld	0.002	0.026	blld	0.091	blld
RE01-MVT-XRF-008	Pine Point	0.122	0.07	blld	0.003	0.024	blld	0.071	blld
RE01-MVT-XRF-009	Pine Point	0.172	0.096	blld	1.058	>1.0	0.830	9.940	8.190
RE01-MVT-XRF-010	Pine Point	5.665	>1.0	2.630	7.608	>1.0	5.830	0.630	0.570
RE01-MVT-XRF-011	Pine Point	6.301	>1.0	3.390	25.061	>1.0	24.110	0.670	0.570
RE01-MVT-XRF-012	Pine Point	80.970	>1.0	47.420	0.059	>1.0	blld	blld	blld
RE01-MVT-XRF-013	Pine Point	0.045	0.078	blld	0.024	0.04	blld	0.171	0.150
RE01-MVT-XRF-014	Pine Point	0.068	0.068	blld	0.129	0.125	0.100	0.362	0.290
RE01-MVT-XRF-015	Rob Lake	0.085	0.069	blld	19.115	>1.0	15.540	6.020	4.090
RE01-MVT-XRF-016	Rob Lake	2.230	>1.0	1.060	6.724	>1.0	5.680	0.580	0.520
RE01-MVT-XRF-017	Rob Lake	0.186	0.175	blld	0.182	0.198	0.110	1.611	1.510
RE01-MVT-XRF-018	Rob Lake	3.433	>1.0	1.850	7.892	>1.0	6.790	0.140	0.120
RE01-MVT-XRF-019	Rob Lake	2.302	>1.0	1.130	3.666	>1.0	3.590	0.140	0.160
RE01-MVT-XRF-020	Rob Lake	0.008	0.017	blld	5.651	>1.0	4.250	0.940	0.640
RE01-MVT-XRF-021	Rob Lake	0.016	0.007	blld	4.449	>1.0	3.140	0.720	0.580
RE01-MVT-XRF-022	Rob Lake	0.401	0.313	blld	14.580	>1.0	10.850	0.250	0.230
RE01-MVT-XRF-023	Rob Lake	1.192	0.721	blld	0.121	0.131	0.080	0.470	0.380
RE01-MVT-XRF-024	Rob Lake	0.100	0.087	blld	0.519	0.481	0.420	2.495	1.780
RE01-MVT-XRF-025	Alberta	0.003	0.003	blld	0.017	0.008	blld	0.102	0.100
RE01-MVT-XRF-026	Alberta	0.052	0.035	blld	28.500	>1.0	19.890	2.140	1.810
RE01-MVT-XRF-027	Alberta	0.002	0.002	blld	2.106	>1.0	blld	0.100	blld
RE01-MVT-XRF-028	Alberta	0.001	0.001	blld	0.021	0.017	blld	0.014	blld
RE01-MVT-XRF-029	Alberta	0.003	0.001	blld	0.004	0.007	blld	blld	blld
RE01-MVT-XRF-030	Alberta	0.003	0.001	blld	0.001	0.007	blld	0.145	0.120
RE01-MVT-XRF-031	Alberta	0.008	0.007	blld	0.003	0.004	blld	1.932	1.140

Continued on next page

Table 3. Geochemical results from laboratory and portable XRF analyzer analyses using powdered samples.

Standard and duplicate samples Sample No.	Certified sample ID or duplicate sample no.	Laboratory ICP-ES Pb (%)	Laboratory XRF Pb (%)	Portable XRF Pb (%)	Laboratory ICP-ES Zn (%)	Laboratory XRF Zn (%)	Portable XRF Zn (%)	Laboratory ICP-ES Fe (%)	Portable XRF Fe (%)
Detection limit ——————————>		0.00002	0.0005	0.1	0.00001	0.0005	0.1	0.000001	0.1
RE01-MVT-XRF-032	MP-1a Cert[1]	3.859	>1.0	3.170	19.115	>1.0	18.060	5.610	5.580
RE01-MVT-XRF-033	Dup-001	0.003	0.008	blld	0.001	0.055	blld	0.095	blld
RE01-MVT-XRF-001		0.002	0.002	blld	blld	0.032	blld	0.092	blld
RE01-MVT-XRF-034	Dup-016	2.192	>1.0	blld	6.576	>1.0	5.560	0.560	0.570
RE01-MVT-XRF-016		2.230	>1.0	1.060	6.724	>1.0	5.680	0.580	0.520
RE01-MVT-XRF-035	Dup-020	0.005	0.014	blld	5.445	>1.0	4.340	0.860	0.720
RE01-MVT-XRF-020		0.008	0.017	blld	5.651	>1.0	4.250	0.940	0.640
RE01-MVT-XRF-036	MP-1a Cert	3.952	>1.0	2.750	19.120	>1.0	17.250	5.740	5.860
RE01-MVT-XRF-037	Dup-024	0.107	0.1	blld	0.584	0.566	0.400	2.500	1.680
RE01-MVT-XRF-024		0.100	0.087	blld	0.519	0.481	0.420	2.495	1.780
RE01-MVT-XRF-038	Dup-025	0.002	0.004	blld	blld	0.022	blld	0.096	0.110
RE01-MVT-XRF-025		0.003	0.003	blld	0.017	0.008	blld	0.102	0.100
RE01-MVT-XRF-039	MP-1a Cert	3.886	>1.0	3.160	18.785	>1.0	17.650	5.700	5.670

[1] CANMET certified sample MP-1a

* blld = below the lower limit of detection

Figure 2. Results of Portable XRF versus laboratory analysis using powdered samples.

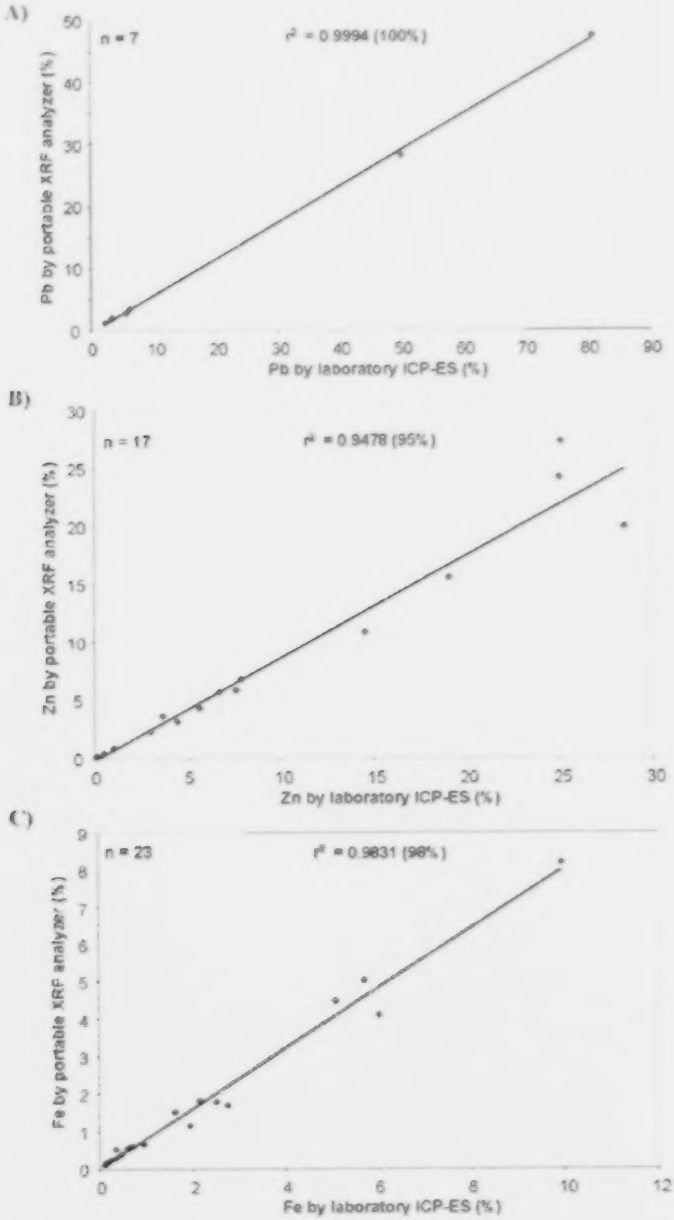
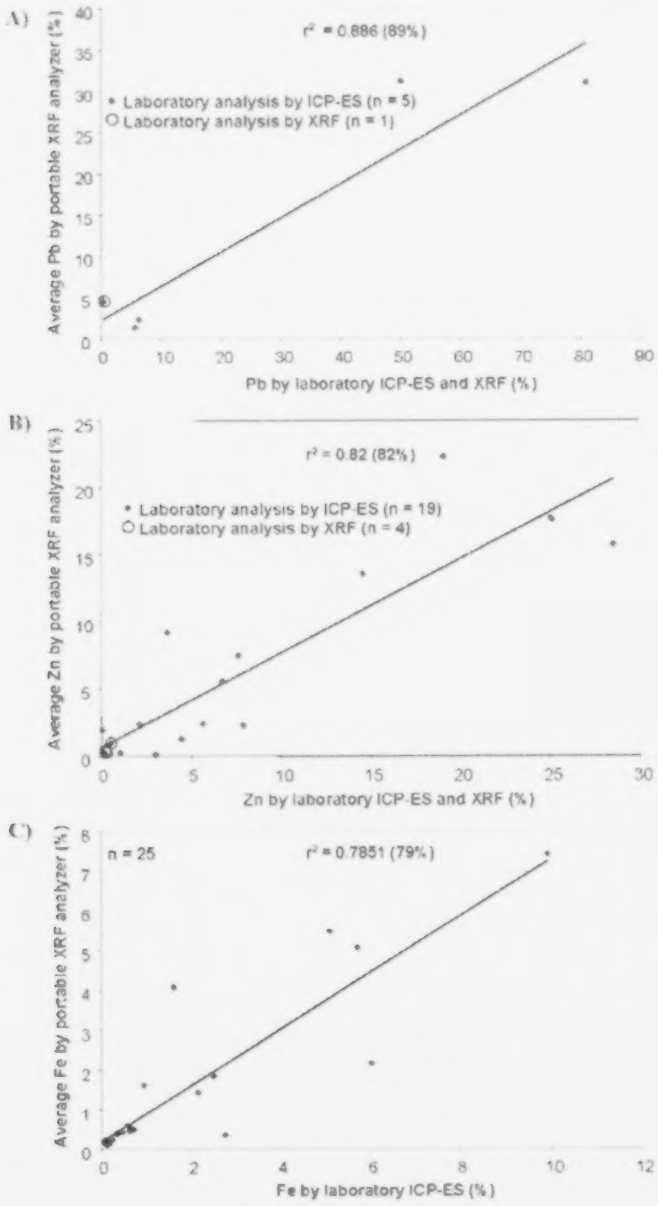


Table 4 Geochemical results from laboratory and portable XRF analyzer spot analyses

Sample No.	Sample location	Laboratory IC_-ES Pb (%)	Laboratory XRF Pb (%)	Portable XRF Pb (%) Spot 1	Portable XRF Pb (%) Spot 2	Portable XRF Pb (%) Spot 3	Portable XRF Pb (%) Spot 4	Portable XRF Pb (%) Avg	Laboratory ICP-MS Zn (%)	Laboratory XRF Zn (%)	Portable XRF Zn (%) Spot 1	Portable XRF Zn (%) Spot 2	Portable XRF Zn (%) Spot 3	Portable XRF Zn (%) Spot 4	Portable XRF Zn (%) Avg	Laboratory ICP-MS Fe (%)	Portable XRF Fe (%) Spot 1	Portable XRF Fe (%) Spot 2	Portable XRF Fe (%) Spot 3	Portable XRF Fe (%) Spot 4	Portable XRF Fe (%) Avg
Detection limit ——————>		0.0002	0.0005	0.1	0.1	0.1	0.1	0.1	0.0001	0.0005	0.1	0.1	0.1	0.1	0.1	0.000001	0.1	0.1	0.1	0.1	0.1
RE01-MVT-XRF-001	NE Ellesmere Island	0.002	0.002	bld*	bld			bld	bld	0.032	bld	bld			bld	0.092	0.180	0.280			0.230
RE01-MVT-XRF-002	NE Ellesmere Island	0.014	0.009	bld	bld	bld		bld	2.997	>1.0	0.110	bld	bld		0.110	2.750	0.350	0.400	0.300		0.350
RE01-MVT-XRF-003	NE Ellesmere Island	bld	0.001	bld	bld			bld	0.019	0.021	bld	bld			bld	5.704	3.470	6.640			5.055
RE01-MVT-XRF-004	NE Ellesmere Island	0.006	0.006	bld	bld			bld	0.007	0.011	bld	bld			bld	5.067	5.780	5.140			5.460
RE01-MVT-XRF-005	Victor Cr., Cornwallis Is.	0.003	0.001	bld	bld			bld	0.001	0.004	bld	bld			bld	0.027	bld	bld			bld
RE01-MVT-XRF-006	Pine Point	50.170	>1.0	30.140	32.140			31.140	25.130	>1.0	17.920	17.220			17.570	0.350	0.330	0.420			0.375
RE01-MVT-XRF-007	Pine Point	0.005	0.016	bld	bld	bld		bld	0.002	0.026	bld	bld	bld		bld	0.091	bld	bld	bld		bld
RE01-MVT-XRF-008	Pine Point	0.122	0.07	bld	bld			bld	0.003	0.024	bld	bld			bld	0.071	0.100	0.230			0.165
RE01-MVT-XRF-009	Pine Point	0.172	0.096	bld	bld			bld	1.058	>1.0	0.210	0.280			0.245	9.940	7.000	7.810			7.405
RE01-MVT-XRF-010	Pine Point	5.665	>1.0	1.340	bld			1.340	7.608	>1.0	10.450	4.460			7.455	0.630	0.340	0.560			0.450
RE01-MVT-XRF-011	Pine Point	6.301	>1.0	2.460	2.180			2.320	25.061	>1.0	18.780	16.590			17.685	0.670	0.390	0.690			0.540
RE01-MVT-XRF-012	Pine Point	80.970	>1.0	41.790	29.310	21.760		30.953	0.059	>1.0	5.610	0.130	0.170		1.970	bld	bld	bld	bld		bld
RE01-MVT-XRF-013	Pine Point	0.045	0.078	bld	bld	bld		bld	0.024	0.04	bld	bld	bld		bld	0.171	0.090	0.150	0.140		0.127
RE01-MVT-XRF-014	Pine Point	0.068	0.068	bld	bld	bld		bld	0.129	0.125	0.180	0.240	bld		0.210	0.362	0.530	0.550	0.170		0.417
RE01-MVT-XRF-015	Rob Lake	0.085	0.069	bld	bld	bld	bld	bld	19.115	>1.0	28.450	25.150	23.970	11.490	22.265	6.020	4.570	2.350	1.490	0.190	2.150
RE01-MVT-XRF-016	Rob Lake	2.230	>1.0	bld	bld	bld	bld	bld	5.724	>1.0	8.670	2.290	7.970	3.180	5.528	0.580	0.390	0.470	1.020	0.510	0.598
RE01-MVT-XRF-017	Rob Lake	0.186	0.175	bld	bld	bld		bld	0.162	0.198	0.120	0.080	0.520		0.240	1.611	2.540	0.960	8.670		4.063
RE01-MVT-XRF-018	Rob Lake	3.433	>1.0	bld	bld			bld	7.892	>1.0	4.120	0.430			2.275	0.140	0.090	0.130			0.110
RE01-MVT-XRF-019	Rob Lake	2.302	>1.0	bld	bld			bld	3.686	>1.0	3.410	14.920			9.165	0.140	0.140	0.140			0.140
RE01-MVT-XRF-020	Rob Lake	0.068	0.017	bld	bld	bld		bld	5.651	>1.0	0.300	1.550	5.370		2.407	0.940	0.990	2.860	0.970		1.607
RE01-MVT-XRF-021	Rob Lake	0.016	0.007	bld	bld			bld	4.449	>1.0	1.100	1.420			1.260	0.720	0.460	0.520			0.490
RE01-MVT-XRF-022	Rob Lake	0.401	0.313	3.480	1.710	8.260	bld	4.483	14.580	>1.0	40.960	2.000	6.580	4.660	13.550	0.250	0.430	0.170	0.160	0.190	0.238
RE01-MVT-XRF-023	Rob Lake	1.192	0.721	bld	bld			bld	0.121	0.131	bld	0.080			0.080	0.470	0.340	0.500			0.420
RE01-MVT-XRF-024	Rob Lake	0.100	0.087	bld	bld			bld	0.519	0.481	0.930	0.990			0.960	2.495	1.060	2.620			1.840
RE01-MVT-XRF-025	Alberta	0.003	0.003	bld	bld	bld		bld	0.017	0.008	bld	bld	bld		bld	0.102	bld	0.120	bld		0.120
RE01-MVT-XRF-026	Alberta	0.052	0.035	bld	bld	bld	bld	bld	28.500	>1.0	7.400	27.540	14.790	13.130	15.715	2.140	2.210	0.700	1.920	0.870	1.425
RE01-MVT-XRF-027	Alberta	0.002	0.002	bld	bld	bld		bld	2.106	>1.0	bld	bld	2.370		2.370	0.100	bld	0.090	0.200		0.145
RE01-MVT-XRF-028	Alberta	0.001	0.001	bld	bld			bld	0.021	0.017	bld	bld			bld	0.014	bld	bld			bld
RE01-MVT-XRF-029	Alberta	0.003	0.001	bld	bld	bld		bld	0.004	0.007	bld	bld	bld		bld	bld	bld	bld	bld		bld
RE01-MVT-XRF-030	Alberta	0.003	0.001	bld	bld	bld		bld	0.001	0.007	bld	bld	bld		bld	0.145	bld	0.100	0.150		0.125
RE01-MVT-XRF-031	Alberta	0.008	0.007	bld	bld	bld		bld	0.003	0.004	bld	bld	bld		bld	1.932	bld	bld	bld		bld

* bld - below the lower limit of detection

Figure 3. Results of Portable XRF spot analysis versus laboratory analysis



In comparison with the ICP-ES technique, a higher percentage of the elements Pb, Zn and Fe were below the limit of detection using the XRF analyzer. For example, Table 3 shows that the ICP-ES technique had one sample (3% of the 31 original samples) analyze below the lower limit of detection for Pb and Zn, and two samples (7%) below the lower limit of detection for Fe. In contrast, the XRF analyzer technique using the powdered samples had 24 (77%), 14 (45%) and 8 (26%) samples below the lower limit of detection for Pb, Zn and Fe, respectively.

Nevertheless, an impressive positive linear correlation is apparent when the results of the portable XRF analysis are plotted versus the ICP-ES analysis (Figures 2 and 3). Their degree of giving comparative results or precision is designated in the scatter plot figures by a linear trend-line and the linear correlation coefficient (r^2), which defines the proportion of the total variability in the response variable that is explained away by knowing the explanatory variable and the best-fit model. Expressed as a percentage, a value of r^2 near 100% represents a strong relationship between the response and explanatory variables, and thus, this will lead to a high prediction of the comparable concentration that will be indicated by either the ICP-ES or XRF analyzer methods.

For example, when compared to laboratory ICP-ES analysis, the Niton portable XRF analyzer 'powder' analysis (Figure 2) is able to record very consistent predictions for Pb, Zn and Fe, with an r^2 between about 95% ($y=0.8807x-0.2567$) and 100% ($y=0.5841x-0.3794$). In comparison, the portable XRF analyzer 'spot' analysis (Figure 3) is less predictive because it only has r^2 values between about 79% ($y=0.7091x+0.1795$) and 89% ($y=0.4132x+2.1888$). A possible explanation for this difference in the quality of the comparative prediction between power and spot analysis is that the prepared powdered sample results were from a considerably more homogeneous sample, both in terms of particle size distribution and element concentration, and consequently, it provides a much higher correlation between the XRF assays and ICP-ES laboratory assays. In contrast, the lower correlation coefficient for the 'spot" or *in-situ* analysis of rocks and cores reflects the relative lack of homogeneity of the mineral elements in these samples. We must also point out that time limitations in our sample methodology did not allow us to conduct spot and powder analysis on the exact same material; rather, separate sample splits were used for the spot and powder analysis. We must report, therefore, that the variation between the spot and powder analyses also may be the result of analysis on different materials. Despite a sample set where the samples do contain a high degree of lithological variation (e.g., zebra dolomite; Table 1), the results of our limited test indicate the Niton portable XRF analyzer may be a useful tool to provide reasonable estimates of the Pb, Zn and Fe content of samples, rather than necessarily always relying on laboratory analyses.

As well, we suggest that part of the deviation from linearity of the Niton portable XRF assays versus the ICP-ES laboratory assays of prepared samples is due to 'matrix effects'; that is, the effects caused by one or a group of elements affecting the results obtained for another element. With specific respect to the portable XRF unit, it cannot determine concentrations of elements below atomic number 18. Consequently, the presence of elements with atomic number below 18, especially if they exist in high concentrations, such as boron, carbon, oxygen, sodium, magnesium, aluminum, silicon and sulphur, may impact the Niton assays where these elements are in matrices associated with sulphides, silicates, carbonates or other compounds comprising elements above this atomic number.

It is recommended, therefore, that Niton XRF analyzer results will be more reliable if they are compared to similar lithological types or mineralogy. For example, we noticed a significant difference in the prediction accuracy of zinc values between the Pine Point and Robb Lake sample sets. Linear correlation coefficient values of 98% ($y=0.6606x+1.2006$) and 81% ($y=1.0372x-0.7504$) were calculated from spot analysis data from the Pine Point and Robb Lake sample areas, respectively. This may indicate that the Robb Lake samples are more mineralogically or lithologically diverse than the suite from Pine Point.

The slope and intercept values of the regression lines from a suite of preliminary comparative assays may be used as 'empirical calibration factors' to 'correct' and thus obtain a better or more comparative Niton XRF result from later analyses. That is, simply by substituting these initial values into the general equation for the regression line (y=mx+c), where *m* is the slope and *c* is the intercept, the values of the subsequent Niton assays (*x*) may be 'corrected' to produce more accurate predictions for the later comparative assays. The Niton units have the facility to enter these empirical calibration factors into the software of the instrument operating in FP mode, such that assays on either prepared samples or spot/in-situ assays in the same or similar matrix will require no further calibration.

Finally, the 'spot' or *in-situ* assays with the Niton portable XRF analyzer may also be used to provide a semi-quantitative identification technique for large 'clusters' of specific mineral assemblages. For example, in sample RE01-MVT-XRF-012, we were able to confirm the tentative visual identification of massive, albeit fine-grained, galena by a spot analysis that reported 81% Pb.

4 Recommendations

Based on the results of this preliminary comparison between a Niton field-portable x-ray fluorescence analyzer and conventional geochemical analysis, we recommend that more rigorous tests of the portable XRF analyzer are warranted. Criteria we wanted to include in this test, but were unable to because of available sample material, relatively short timeframe and location, include

1) a variety of rock lithologies (e.g., sedimentary and volcanic rock types), and metallic mineral and energy commodities (e.g., sedimentary exhalative sulphides, sandstone uranium and oil sands);
2) a more stringent sample preparation methodology, where the identical sample is crushed to various size fractions and analyzed; this would test our hypothesis that the crushed and powdered material are more likely to provide more accurate results; and
3) operate the XRF analyzer in both 'high range' and 'low range' modes for element concentration assays.

5 Conclusions

An analytical test to evaluate the quantitative measuring comparability of the Niton field-portable x-ray fluorescence (XRF) versus conventional geochemical analytical methods showed good results. The XRF analyzer technique exhibited a high analytical precision for the elements Pb, Zn and Fe from the sample set selected for this test. For example, when compared with ICP-ES analysis, a linear correlation coefficient (r^2) of between 95% and 100% was determined for powdered XRF analysis and an r^2 of between 79% and 89% for spot XRF analysis. We conclude, therefore, that the Niton XRF analyzer can produce quick and efficient screening assays and analytical results of greater precision by powdering approximately 10 g of the sample. As well, the precision may be further enhanced by the use of "empirical correction factors" that can be entered into the Niton instrument in order to improve the predictive assays for later samples with comparative mineralogy.

Some limitations of the Niton portable XRF instrument in the FP operation mode, used for this test, include that the limit of detection in this mode is generally higher than most conventional geochemical analysis and, therefore, the instrument reports only a few elements with analytical certainty. In this test, for example, the XRF analyzer reported only Pb, Zn and Fe at concentrations greater than (>) 0.1 % within the 95% confidence band of the instrument. As geochemical assessments generally require information about as many elements as possible, with results ranging from percentage down to parts per million level or less, the XRF analyzer may need to be operated in both FP and CN modes for use in multi-element reconnaissance surveys. Having said this, it really is dependent on the needs of the survey.

Thus, for example, if a geochemical assessment was focused mainly on base metals (e.g., Pb and Zn) where economic ore element concentration levels are >0.5%, then the Niton portable XRF analyzer would analyze a vast amount of rock (or core) in a timely and cost-efficient manner.

Lastly, as the portable XRF analyzer technology evolves and improves, it is probable that a higher number of elements with lower limits of detection will become available. As a result, the tool will become more useful in reconnaissance-type fieldwork. As well, it will have significant benefit in core libraries, especially if obtaining real-time geochemical analytical results can be coupled with lithological and mineralogical core logging.

6 References

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Turner, A. and McPhee, D. (1994): Analyses of Paleozoic core data for the evaluation of potential Pb-Zn mineralization in northeastern Alberta; Alberta Energy, Alberta Geological Survey, Open File Report 1994-18, 51 p.